ELECTROCHEMICAL SYNTHESIS OF PEROXYACETIC ACID ON PT/PTO AND PBO_2 ANODES

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1. Introduction.

Peroxyacetic acid (PAA) is a strong disinfectant with a wide spectrum of antimicrobial activity. It has been widely used in medical and hygiene fields, and disinfection of wastewater. Recently, PAA emerges as alternative to conventional chlorine containing chemicals in the effort to develop a more environmentally friendly bleaching process in pulping and paper-making industry. It is also an excellent active reagent for epoxidation of unsaturated triglycerides for obtaining of low cost plasticizers with good performance from natural and renewable sources. PAA is produced on an industrial scale by chemical synthesis through the interaction of concentrate acetic acid with the concentrate peroxide of hydrogen (60…80%) with an application of oxygen catalyst.

2. Research methodology.

The current-voltage curves were obtained with the potentiostat P-45X. There are two types of anodes: 1) platinum plate; 2) Titanium current lead with RuO_2 sublayer and covered by PbO_2 with an active surface about 1.1 sm^2. Side and back surface of anodes were isolated. Auxiliary electrode was made from platinum. The silver chloride electrode was applied as the reference one.

3. Results and Discussion.

The direction of anodic processes in the acetic solution depends on the numerous conditions of process. The largest impact have the pH of electrolyte, anodic material, anodic potential, temperature [7-9]. Electrochemical synthesis of PAA is the result of oxidation of acetic acid molecules:

$$CH_3COOH + H_2O = CH_3COOOH + 2H^+ + 2e^-,\ E^0_{CH_3COOH/CH_3COOOH} = 1.8186\ \text{V}. \quad (1)$$

To perform the electrochemical synthesis of PAA we apply water solutions of acetic acid with the concentration about 0.5...9.0 mol·dm^{-3}. In the water solutions of acetic acid the oxidation of water is combined anodic process with (1):

$$2H_2O = O_2 + 4H^+ + 4e^-,\ E^0_{H_2O/O_2} = 1.228\ \text{V} \quad (2)$$

$$2H_2O = H_2O_2 + 2H^+ + 2e^-,\ E^0_{H_2O/H_2O_2} = 1.776\ \text{V} \quad (3)$$

Electrochemical synthesis of hydrogen peroxide can be performed only at temperatures under 290…295 K. To achieve the required anodic potentials for processes (1) and (3) we should apply the material with the high oxygen overvoltage. Platinum and lead-dioxide anode were used for research the kinetics of anodic process in water acetic water solution.

Increase of the acetic acid concentration leads to the significant shift of potential into positive area on Pt/PtO anode. It can be explained by the influence of acetic acid concentration on the adsorption on Pt/PtO surface. Acetic acid doesn't make an influence on the electrochemical process on PbO_2 anodes at the concentrations from 1 to 6 mol·dm^{-3}. The current rise for acetic acid (C=0,5 mol·dm^{-3}) begins at 1.0…1.1 V and higher. These values correlates with an oxygen release. The further rise of anodic potential creates the necessary conditions for H_2O_2 and PAA formation. Presence of H_2O_2 and PAA was proved by results by iodometric titration. The current rise for concentrated acetic acid (C = 1…9 mol·dm^{-3}) starts at 1.6…1.8 V and is followed by formation of H_2O_2 and PAA. It is also well-known that Pt/PtO anodes are catalysts for hydrogen peroxide destruction. Electrochemical synthesis of PAA on the Pt/PtO anode proceeds through the following stages:

$$Pt/PtO + H_2O \rightarrow Pt/PtO(OH\cdot) + H^+ + e^-; \quad (4)$$

$$Pt/PtO(OH\cdot) + CH_3COOH \rightarrow Pt/PtO + CH_3COOOH + H^+ + e^-. \quad (5)$$

The current rise on PbO_2 anode surface in 0.5…9.0 mol·dm^{-3} acetic solution starts at 1.4…1.5 V. The current rise on PbO_2 anode surface in 0.5…9.0 mol·dm^{-3} acetic solution starts at 1.4…1.5 V and higher and is accompanied by the oxygen release. The rise of anodic potentials from 1.8…1.9 V and higher leads to the formation of H_2O_2 and PAA. Concentration of acetic acid on PbO_2 surface doesn't make a significant influence. Considering this, it should be concluded the adsoption

of acetic molecules on the surface of PbO_2 anode is quite weak. Therefore, the radical OH· particles can be formed on PbO_2 surface and be involved into PAA formation:

$$H_2O \rightarrow OH\cdot + H^+ + e^-; \quad (6)$$

$$OH\cdot + CH_3COOH \rightarrow CH_3COOOH + H^+ + e^-. \quad (7)$$

At the potentials higher than 2.2…2.3 B the following reactions can be performed: the Kolbe reaction; reactions of anodic displacement and addition; destructive oxidation of acetic acid [8-9]. Electrochemical synthesis of PAA is impractical in these conditions. Synthesis of PAA should be performed in the range of anodic current density 50…150 $A \cdot m^2$.

The further research was conducted with application of water solution (3 $mol \cdot dm^{-3}$) of acetic acid. The specific conductivity of water acetic solution is $\kappa = 1.55 \cdot 10^3$ Sm/sm [9]. Sulphuric acid with concentration about 0,5 $mol \cdot dm^{-3}$ was chosen as a conductive admixture and was added into acetic solution. According to the results of research electrochemical synthesis of PAA should be performed in the range of current densities from 500 to 1500 $A \cdot m^2$, where the maximal current output can be reached. Application of PbO_2 as anodic material for synthesis of PAA was more effective comparing to the Pt/PtO. The efficiency was estimated by the current output value which is higher on the PbO_2 anodes. Addition of the sulphuric acid makes the catalytic effect in the electrochemical synthesis of PAA.

The study of adsorption of acetic acid on Pt/PtO and PbO_2 anodic surface was conducted in the water acetic solution ($C = 10^{-2}$ $mol \cdot dm^{-3}$) with addition of 0,01 M H_2SO_4. Considering the geometry of anode there was calculated an adsorption of acetic molecules, $mol \cdot dm^{-3}$: Pt/PtO – $2…8 \cdot 10^{-6}$; PbO_2 – $3…7 \cdot 10^{-8}$. The higher adsorption on platinum surface proves the mechanism (4) – (5), and the low adsorption on PbO_2 surface with the current output of PAA (for Pt/PtO – 0.12%, for PbO_2 – 0.36%) correlates with the mechanism (6). Anodic process of PAA formation can be intensified by applying the peroxide-particles as promoters in the electrolyte. Polarization curves were obtained in 3 $mol \cdot dm^{-3}$ CH_3COOH + 0.5 M H_2SO_4 with addition of CNS^-, I^-, Cl^-, Br^-, F^-. Ions were added with the appropriate salts of alkaline metals. Addition of CNS^-, I^-, Cl^-, Br^-, F^- leads to the braking of combined anodic process – oxygen release. The most effective admixtures for Pt/PtO are I^-, Cl^- (Current output is 1.2…1.5%); for PbO_2 – addition of I^-, F^- (Current output is 0.50…0.55%). Addition of CNS^- was defined as impractical. The concentration of PAA, obtained by electrochemical synthesis correlates with the concentration of PAA in disinfectant solution: in medicine (0,1%), at poultry farms (0.02…0.03%), in dairy industry (0.015…0.025%).

5. Conclusions.

The possibility of electrochemical synthesis of PAA, which can be applied in different branches of industry, was shown. Stages of electrochemical formation of PAA on Pt/PtO and PbO_2 anodic surfaces were performed. Acetic acid molecules are oxidized through through the interaction with radical OH particles on the anodic surface.

It was shown that the addition of 0,5 mol·dm^{-3} sulphuric acid makes the catalytic effect in the electrochemical synthesis of PAA. Application of PbO_2 in anodes is much more effective comparing to the Pt/PtO. The range of current densities 500…1500 A/m^2 was defined as the most expedient in the electrochemical synthesis of PAA. Addition of CNS^-, I^-, Cl^-, Br^-, F^- ions brakes the combined anodic process which is oxygen release. For Pt/PtO the most effective admixtures are I^-, Cl^- (Current output is 1.2…1.5%); for PbO_2 – I^-, F^- (current output is 0.50…0.55%). Addition of CNS^- is impractical.

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